

Docket No.: 491712000100

(PATENT)

#### IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:

Eugene S. SMOTKIN

Application No.: 09/891,200

Filed: June 26, 2001

For: ELECTROLYTE COMPONENTS FOR USE IN

**FUEL CELLS (AS AMENDED)** 

Confirmation No.: 9382

Art Unit: 1745

Examiner: Raymond Alejandro

# <u>UNDER 37 C.F.R. § 1.132</u>

Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450

Dear Sir:

- I, Eugene S. Smotkin, declare as follows:
- 1. I am the inventor of the subject matter set forth and claimed in the above-referenced application. I have been in the business of designing and evaluating fuel cells for over 10 years. A copy of my *curriculum vitae* is attached.
- 2. This declaration is intended to clarify the technology related to the invention described and claimed. It includes subject matter that is well known to the practitioner of the art and that may be helpful to the Office in evaluating the technical features of the invention.

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## 3. As a preliminary matter, I note the following information:

voltage drop

The variables required for discussion of the area specific resistance (ASR) of proton conducting membranes for fuel cells, and their associated units, are given in Table 1.

**Symbol** Units Variable R resistance  $\Omega$  (Ohms) S (Siemens) conductance  $1/\Omega$ S/cm (Siemens/cm) conductivity σ thickness L cm cm<sup>2</sup> Α area  $\Omega$  cm<sup>2</sup> (Ohm cm<sup>2</sup>) area specific resistance **ASR** A (ampere) i current A/cm<sup>2</sup> (ampere/cm<sup>2</sup>) current density

TABLE 1

For a proton conducting membrane of thickness L and conductivity  $\sigma$ , the ASR is defined as their ratio.

 $\Delta V$ 

volts

$$ASR = \frac{L}{\sigma} \tag{1}$$

The voltage drop across an electrolyte is equal to the current density times the area specific resistance, according to the equation.

$$\Delta V = j \times ASR \tag{2}$$

Thus, the ASR of the membrane is the quantity that determines the magnitude of the voltage drop at a given current density. The voltage drop corresponds to loss in energy efficiency of the cell, and therefore it is a quantity that should be minimized in fuel cells. Therefore, the ASR must be low enough to provide for a small  $\Delta V$ .

4. Nafion<sup>®</sup> 117, a proton-conducting polymer membrane commonly used as an electrolyte in fuel cells, is generally employed with a thickness of 1.78x10<sup>-2</sup> cm. At 80°C, the

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protonic conductivity ( $\sigma$ ) of Nafion<sup>®</sup> is  $1.19 \times 10^{-1}$  S/cm, thus, its ASR is  $0.15 \Omega$ .cm<sup>2</sup> at this thickness (see Equation (1)). Nafion<sup>®</sup> 117 is a good metric for comparison of new electrolyte membranes under development for fuel cells, because the voltage drop it creates at ordinary current densities (0.5 A/cm<sup>2</sup>) is approximately 75 mV. Membranes with higher ASR values would give higher values of  $\Delta V$ , resulting in unacceptably large efficiency losses in the fuel cell (see Equation (2)).

- 5. The attached Figure 1 (which corresponds to Figure 10 of the present application) shows the variation at 80°C of the ASR of Nafion® 117 with thickness for L values between 25 and 250 microns. The thickness dependence of the ASR of a hypothetical electrolyte membrane consisting of an inorganic electronically insulating proton conductor (EIPC) of lower conductivity than Nafion® 117 is also shown in the graph for comparison. The hypothetical EIPC has  $\sigma = 1 \times 10^{-4}$  S/cm at 250°C, which is a typical value for inorganic proton conductors. Values of ASRs for the hypothetical EIPC at temperatures where the conductivity has this value with L values between 0.02 to 76 microns are shown in the plot. The horizontal line indicates the thickness of the inorganic EIPC that would have the same ASR (0.15  $\Omega$ .cm²) as Nafion® 117 with a thickness of 178  $\mu$  at 80°C. According to equation (1), in order for the hypothetical EIPC to have ASR = 0.15  $\Omega$ .cm², its thickness would have to be only 0.15 microns.
- 6. If the temperature dependencies of  $\sigma$  for candidate EIPCs (e.g., ammonium polyphosphate and BCN18) are known, the thickness required for an ASR of 0.15  $\Omega$ .cm<sup>2</sup> (i.e., to match the performance of 178  $\mu$  thick Nafion®) at any temperature can be calculated. The variation of conductivity with temperature for many of the candidate protonic conductors is available in the literature. Given the values of  $\sigma$  as a function of temperature and the desired ASR value of 0.15  $\Omega$  cm<sup>2</sup>, the thicknesses for candidate EIPCs can be calculated from equation (1).

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7. Figure 2 (identical to Figure 4 of the application) shows the desired membrane thicknesses of these candidate protonic conductors as a function of temperature. In all cases, very thin EIPC membranes (less than 10 micron thickness) will be needed to match the ASR of Nafion<sup>®</sup> 117. I have found that such thin membranes of inorganic ceramic materials are not mechanically strong enough to withstand the stresses that are applied in the assembly of a fuel cell, and thus a support structure is needed.

8. I have found a way to employ materials that ordinarily would not be practical for use in fuel cells to serve this purpose by finding a way to employ them at thicknesses where the ASR value is satisfactory. This has been accomplished by supporting these materials on a metal/metal hydride support which is conductive for protons as well as electrons. The conductivity for electrons does not adversely affect the ability of the supported electrolyte to function in a fuel cell, as it, itself, provides the resistance to electrons required.

I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful, false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Executed at POWN POINT, IN, on 9 JAN 2006.

(city) (state) (Eugene S. Smotkin)

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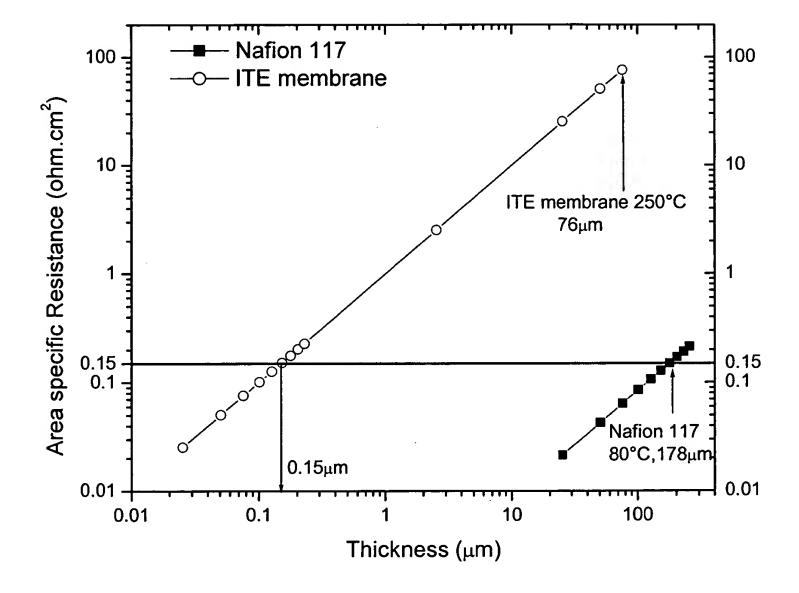


Figure 1. ASR of the Intermediate Temperature Electrolyte Membrane (ITE Membrane) compared to conventional Nafion® 117. To achieve the same ASR (indicated by a horizontal line at 0.15 ohm cm²), the thickness of ITE membrane is 0.15 microns, compared to 178 microns for Nafion®.

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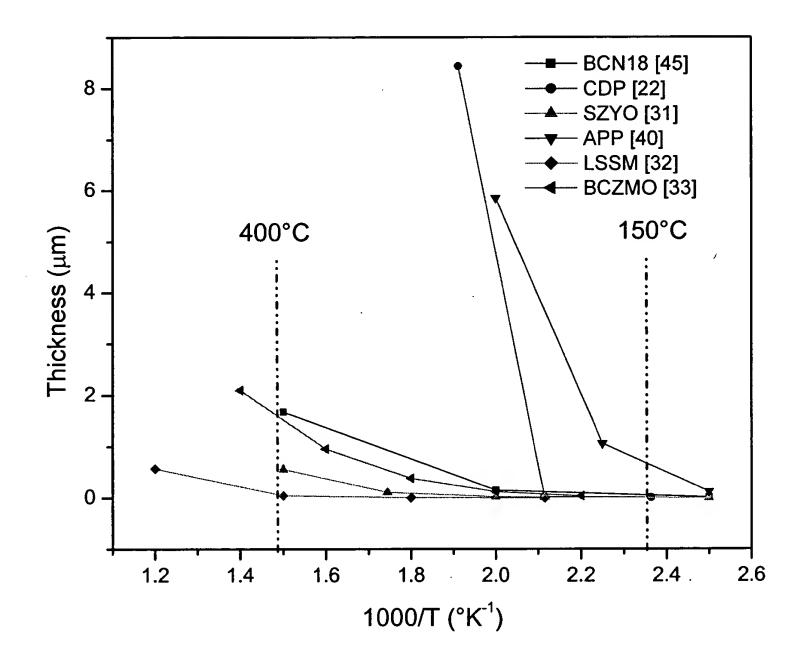


Figure 2. Required thickness (in microns) of EIPCs as a function of reciprocal temperature. The temperature range between 150° and 400°C is bracketed by the dot-dash lines.

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## **Eugene S. Smotkin**

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#### **Education**

B.Sc., Chemistry, San Jose State University, 1977; M.S., Chemistry, San Francisco State University, 1984; Ph.D., Chemistry, with A. J. Bard & M. A. Fox, University of Texas at Austin, 1989

## Work experience:

Professor of Chemistry at The University of Puerto Rico at Rio Piedras, 2002-present; Research Professor of Chemical Engineering at University of Notre Dame, 2004-present; Joint Associate Professor of Chemistry and Chemical Engineering at Illinois Institute of Technology, 1998-2002; Assistant Professor of Chemistry at IIT, 1992-1998

#### Research interests

Catalysis, PEM Fuel Cells, Physical Electrochemistry, Reaction Engineering, Mass Spectrometry, Combinatorial Materials Discovery, Applied Quantum mechanics

## Selected professional activities

1999, Workshop Chair and Organizer: ARO Workshop on Designed Catalysts for Fuel Processors and Fuel Cells, Chicago, IL April 18-21, 1999

1999, Founder of NuVant Systems Inc.

2002, Symposium Chair and Organizer at Orlando 223rd ACS National Meeting, Electrocatalysis and Fuel Cells, April 7-11, 2002

2006, Chair and organizer of the 4<sup>th</sup> U.S.-Japan workshop on Combinatorial Materials Science & Technology, San Juan, PR, December 6-9, 2006

## **Key Lectureships**

Heyrovsky Discussions, Heyrovsky Institute, Prague, Czech Republic, 2005 Gordon Conference, Bristol, RI, 2004

Olaf A. Hougen Lecturer, University of Wisconsin Hougen Symposium, 2003

US Army Research Office, Theory and Surface Measurements of Fuel Cell Catalysts Workshop, Denmark, 2003.

Gordon Conference, New London, NH, 1999

Gordon Conference, Ventura, CA, 1999

#### **Patents**

- 1. E. S. Smotkin "Heat Activated Membrane Introduction Apparatus and Method for Screening Materials" U.S. Patent 6,923,939 B1, 2005
- 2. E. S. Smotkin, "High throughput screening device for combinatorial chemistry" U.S. Patent 6,692,856 B2, **2004**
- 3. T. E. Mallouk, E. S. Smotkin, B. C. Chan, E. Reddington, B. Gurau, R. Viswanathan, A. Sapienza, R. Liu, and G. Chen, "Electrocatalyst Compositions," U.S. Patent

- 6,284,402, 2001.
- 4. E. S. Smotkin, et al., "Single Phase Ternary Pt-Ru-Os Catalysts for Direct Oxidation Fuel Cells" U.S. Patent 5,856,036, 1999
- 5. E. S. Smotkin, et al., "Hybrid Electrolyte System" U.S. Patent 5,846,669, 1998
- 6. E. S. Smotkin, A. J. Bard and M. A. Fox, "Photoelectrochemical Cell for Unassisted Photocatalysis and Photosynthesis," U.S. Patent 4,793,910, 1988
- 7. E. S. Smotkin, "Hydrogen permeable membrane for fuel cells, and partial reformate fuel cells" USP 20020031695, pending

#### **Publications**

- 1. Rukma Basnayake, Zhengrong Li, Srilakshmi Katar Zhou, Eugene S. Smotkin, Dominick J. Casadonte, Jr, Carol Korzeniewski, Sonochemistry as a Route to the Preparation of PtRu Nanoparticles with Bulk Alloy Properties, Chemistry of Materials, submitted, (2005)
- 2. Maria Salazar, Eugene Smotkin, "Proton spillover promoted olefin isomerizations at polymer electrolyte fuel cell cathodes", Journal of Applied Electrochemistry, in press (2005)
- 3. Eugene S. Smotkin' Junhua, Jiang, Amit Nayar, Renxuan Liu, "High-throughput screening of fuel cell electrocatalysts" Applied Surface Science, In press, (2005)
- 4. P. K. Babu, H. S. Kim, S. T. Kuk, J. Ho Chung, Eric Oldfield, Andrzej Wieckowski, E. S. Smotkin, "Activation of Nanoparticle Pt-Ru Fuel Cell Catalysts by Heat Treatment: A 195Pt NMR and Electrochemical Study", J. Phys. Chem. B.; 109(36); 17192-17196 (2005).
- 5. N. Dimakis, H. Iddir, R. R. Díaz-Morales, Renxuan Liu, Grant Bunker, Eun-Hyuk Chung and E. S. Smotkin "A Band Dispersion Mechanism for Pt Alloy Compositional Tuning of Linear Bound CO Stretching Frequencies", J. Phys. Chem. B, 109, 1839-1848 (2005)
- 6. B. C. Chan, R. Liu, K. Jambunathan, H. Zhang, G, Chen, T. E. Mallouk, and E. S. Smotkin, "Comparison of High Throughput Electrochemical Methods for Testing Direct Methanol Fuel Cell Anode Electrocatalysts," J. Electrochem Soc, 152, A594-A600 (2005)
- 7. R. R. Díaz-Morales, R. Liu, E. Fachini, G. Chen, Carlo U. Segre, Antonio Martínez, Carlos Cabrera, and Eugene S. Smotkin "XRD and XPS Analysis of As-Prepared and Conditioned DMFC Array Membrane Electrode Assemblies" J. Electrochem. Soc. 151, A1314 (2004)
- 8. A. Nayar, Y. Kim, J. Rodriguez, R. Willis, D. Galloway, F. Falih, and E. Smotkin, "High Speed Laser Activated Membrane Introduction Mass Spectrometric Evaluation of Bulk Methylcyclohexane Dehydrogenation Catalysts" Applied Surface Science, 223, (2004), 118-123
- 9. T. E. Mallouk and E. S. Smotkin "Combinatorial Catalyst Development Methods" Vol 2, part 3, pp 334 347, In Handbook of Fuel Cells Fundamentals, Technology and Applications, Edited by Wolf Vielstich, Arnold Lamm, Hubert A. Gasteiger, John Wiley & Sons, LTD, Chichester, (2003)
- 10. Eugene S. Smotkin and Robert R. Diaz-Morales, "New Electrocatalysts by Combinatorial Methods" in Annual Reviews of Material Research, 33, pp 557 579 (2003)
- 11. Bogdan Gurau, E. S. Smotkin, "Methanol Crossover in Direct Methanol Fuel Cells: A Link Between Power and Energy Density" Journal of Power Sources 112, (2002) 339-352
- 12. Renxuan Liu, E. S. Smotkin, "Array Membrane Electrode Assemblies For High Throughput Screening of Direct Methanol Fuel Cell Catalysts" Journal of Electroanalytical Chemistry, 535, (2002) 49-55
- 13. Amit Nayar, Renxuan Liu, Robert J. Allen, Michael J. McCall, Richard R. Willis, and Eugene S. Smotkin, "Laser-Activated Membrane Introduction Mass Spectrometry for High-

- Throughput Evaluation of Bulk Heterogeneous Catalysts" Analytical Chemistry, 74, 9, (2002) 1933-1938
- 14. Ramesh Viswanathan, Renxuan Liu and Eugene S. Smotkin, "In-situ X-ray Absorption Fuel Cell" Review of Scientific Instruments, Vol. 73, Issue 5, (2002), 2124-2127
- 15. Han-Wei Lei, Sanghyuk Suh, Bogdan Gurau, Bizuneh Workie, Renxuan Liu, Eugene S. Smotkin, "Deuterium Isotope Analysis of Methanol Oxidation on Mixed Metal Anode Catalysts" Electrochimica Acta, 47, (2002) 2913-2919
- 16. Yong-Tae Kim and Eugene S. Smotkin, "The Effect of Plasticizers on Transport and Electrochemical Properties of PEO-based Electrolytes for Lithium Rechargeable Batteries" Solid State Ionics, 149, (2002) 29-37
- 17. S. Sanicharane, Aili Bo, Bhaskar Sompalli, Bogdan Gurau, Eugene S. Smotkin, "In-situ 50°C Tandem Surface Reflective/Exhaust-Transmission Spectroscopy of Direct Methanol Fuel Cell Membrane Electrode Assemblies" J. Electrochem. Soc. 149, (5), A554-A557, (2002)
- 18. Rameshkrishnan Viswanathan, Guoyan Hou, Renxuan Liu, Simon R. Bare, Frank Modica, George Mickelson, C. U. Segre, Nadia Leyarovska, Eugene S Smotkin, "In-situ XANES Study of Carbon Supported Pt-Ru Anode Electrocatalysts for Reformate-Air Polymer Electrolyte Fuel Cells" J. Phys. Chem. B, Vol. No. 106, Issue 13 3458-3465 (2002)
- 19. Frank E. Jones III, Stephen B. Milne, Bogdan Gurau, Eugene S. Smotkin, Stuart R. Stock, and C. M. Lukehart, "Synthesis and Characterization of PtSn/Carbon and Pt3Sn/Carbon Nanocomposites as Methanol Electrooxidation Catalysts" Journal of Nanoscience and Nanotechnology, Vol. 2, No 1, 81-87 (2002)
- 20. Zhijie Liu, Robert G. Arnold, Eric A. Betterton, and Eugene Smotkin "Reductive Dehalogenation of Gas-Phase Chlorinated Solvents Using a Modified Fuel Cell", Environmental Science & Technology; (2001); 35(21); 4320-4326.
- 21. D. E. Fremgen, E. S. Smotkin, R. E. Gerald III, R. J. Klingler and J. W. Rathke "Microemulsions of water in supercritical carbon dioxide: an in-situ NMR investigation of micelle formation and structure", The Journal of Supercritical Fluids, Volume 19, 287-298 (2001)
- 22. Lloyd Ploense, Maria Salazar, Bogdan Gurau, E. S. Smotkin, "Spectroscopic study of NEMCA Promoted Alkene Isomerizations at PEM Fuel Cell Pd-Nafion Cathodes," Solid State Ionics 136-137 (0); 713-720 (2000)
- 23. A. Bo, S. Sanicharane, Bhaskar Sompalli, Qinbai Fan, Bogdan Gurau, Renxuan Liu, and E. S. Smotkin, "In Situ Stark Effects with Inverted Bipolar Peaks for Adsorbed CO on Pt Electrodes in 50°C Direct Methanol Fuel Cells", J. Phys. Chem. B; 104 (31); 7377-7381 (2000)
- 24. R. C. Binning, Jr., Meng-Sheng Liao, Carlos Cabrera, Yasuyuki Ishikawa, Hakim Iddir, Renxuan Liu, E. S. Smotkin, Antonio J. Aldykiewica, Jr., Deborah J. Meyers, "Density Functional Calculations on CO Attached to PtnRu(10-n) (n = 6 10) Clusters" International Journal of Quantum Chemistry, 77, 589-598 (2000)
- 25. R. Liu, Hakim Iddir, Qinbai Fan, Guoyan Hou, Aili Bo, Kevin L. Ley, E. S. Smotkin, Y. Sung+, H. Kim, S. Thomas, A. Wieckowski "Potential Dependent Infrared Absorption Spectroscopy of Adsorbed CO and X-ray Photoelectron Spectroscopy of Arc-melted Single Phase Pt, PtRu, PtOs, PtRuOs and Ru Electrodes," J. Phys. Chem. B, 104, 3518-3531 (2000)
- 26. B. K. Mandal, C. J. Walsh, T. Soolsimuang, S. J. Behroozi, Sangu-gu Kim, Yong-Tae Kim, E. S. Smotkin, R. F. Filler and Cathy Castro, "New Class of Single Ion-Conducting Solid Polymer Electrolytes Derived from Polyphenols" Chemistry of Materials, 12, 6-8, (2000)
- 27. E. Reddington, J.-S. Yu, A. Sapienza, B. C. Chan, B. Gurau, R. Viswananthan, R. Liu, E. S. Smotkin, S. Sarangapani and T. E. Mallouk, "Combinatorial Discovery of and Optimization

- of New Electrocatalysts," Combinatorial Chemistry: A Practical Approach, H. Fenniri, Ed., Oxford University Press, Oxford, UK, pp. 401 420 (2000)
- 28. E. Reddington, J.-S. Yu, A. Sapienza, B. C. Chan, B. Gurau, R. Viswanathan, R. Liu, E. S. Smotkin, S. Sarangapani, and T. E. Mallouk, "Combinatorial Screening of Anode and Cathode Electrocatalysts for Direct Methanol Fuel Cells," in Advanced Catalytic Materials, Lednor, P.; Nakagi, D.; Thompson, L. T., Eds., MRS Symp. Proc. v. 549, pp. 231-236 (1999)
- 29. B. Gurau, R. Viswananthan, R. Liu, T. J. Lafrenz, K. L. Ley, and E. S. Smotkin, "Structural and Electrochemical Characterization of Binary, Ternary, and Quaternary Platinum Alloy Catalysts for Methanol Electro-oxidation," J. Phys. Chem. B, 102, 9997-10003, (1998)
- 30. L. Liu, R. Viswananthan, R. Liu, E.S. Smotkin, "Methanol Oxidation on Nafion Spin-Coated Polycrystalline Platinum and Platinum Alloys," Electrochemical and Solid-State Lett., 3, 123-125 (1998)
- 31. E. Reddington, A. Sapienza, B. Gurau, R. Viswananthan, S. Sarangapani, E. S. Smotkin, T. E. Mallouk, "Combinatorial Electrochemistry: A Highly Parallel, Optical Screening Method for the Discovery of Better Electrocatalysts", Science, 280, 1735 1739 (1998)
- 32. L. Liu, C. Pu, R. Liu, Qinbai Fan, E. S. Smotkin, "Carbon Supported Vs Unsupported Pt/Ru Anodes for Liquid Feed Methanol Fuel Cells," Electrochimica Acta, 43, 3657-3663 (1998)
- 33. L. Ploense, M. Salazar, Bogdan Gurau and E. S. Smotkin, "Proton Spillover Promoted Isomerization of n-Butylenes on Pd-Black Cathodes/Nafion 117," J. Am. Chem. Soc., 119, 11550-11551 (1997)
- 34. R. Liu, K. Triantafillou, L. Liu, C. Pu, E. Smotkin, "Coulometrically Normalized RDE Evaluation of High Surface Area Methanol Anode Catalysts," J. Electrochem. Soc, 144, L148 L150 (1997)
- 35. K. L. Ley, R. Liu, C. Pu, Qinbai Fan, Nadia Leyarovska, Carlo Segre and E. S. Smotkin, "Methanol Oxidation on Single Phase Pt-Ru-Os Ternary Alloys," J. Electrochem. Soc, 144, 1543-1549 (1997)
- 36. Q. Fan, Cong Pu and E. S. Smotkin, "In-Situ FTIR-Diffuse Reflection Spectroscopy of Direct Methanol Fuel Cell Anodes and Cathodes," J. Electrochem. Soc., 143, 3053-3057 (1996)
- 37. Q. Fan, Cong Pu, K. L. Ley and E. S. Smotkin, "In-Situ FTIR-Diffuse Reflection Spectroscopy of the Anode Surface in a Direct Methanol/Oxygen Fuel Cell," J. Electrochem. Soc., 143, L21- L23 (1996)
- 38. Cong Pu, Wenhua Huang, K. L. Ley and E. S. Smotkin, "A Methanol Impermeable Proton Conducting Composite Electrolyte System," J. Electrochem. Soc., 142, L119-L120 (1995)
- 39. E. S. Smotkin and G. A. Rechnitz, "Electrochemical Determination of Tricyclic Antidepressants," Analytical Letters, 24, 797-808, (1991)
- 40. S. Cervera-March and E. S. Smotkin, "Photoelectrode Array System for Hydrogen Production from Solar Water Splitting," International Journal of Hydrogen Energy, 4, 243-247 (1991)
- 41. E. S. Smotkin, F. T. Moy, W. Z. Plachy, "Dioxygen Solubility in Aqueous Phosphotidylcholine Dispersions," Biochimica Et Biophysica Acta, 1061, 33-38 (1991)
- 42. E. S. Smotkin, R. M. Brown, L. K. Rabenburg, K. Salomon, A. J. Bard, A. Campion, M. A. Fox, T. E. Mallouk, S. E. Webber and J. M. White, " *Ultra small Particles of CdSe and CdS Formed in Nafion by an Ion-dilution Technique*," **J. Phys. Chem.** 94, 7543-7548 (1990)
- 43. William Z. Plachy, Frederick T. Moy, Eugene S. Smotkin and Mary E. Hatcher "Oxygen in lipids and in skin: solubility and diffusion coefficients," Free Radical Biology and Medicine, Volume 9, Supplement 1, 1990, Page 120 (1990)

- 44. S. Cervera-March, E. S. Smotkin, A. J. Bard, A. Campion, M. A. Fox, T. E. Mallouk, S. Webber and J. M. White, "Modeling of Bipolar Semiconductor Photoelectrodes and Multielectrode Arrays for Unassisted Water Splitting". J. Electrochem. Soc., 135, 567-573 (1988)
- 45. E. S. Smotkin, C. Lee, A. J. Bard, A. Campion, M. A. Fox, T. E. Mallouk, S. Webber and J. M. White, "Size Quantization Effects in CdS Layers Formed by a Langmuir Blodgett Technique", Chem. Phys. Lett. 152, 265-268 (1988)
- 46. E. S. Smotkin, S. Cervera-March, A. J. Bard, A. Campion, M. A. Fox, T. E. Mallouk, S. Webber and J. M. White, "Bipolar CdSe/CoS Semiconductor Photoelectrodes Arrays for Photolytic Water Splitting". J. Phys. Chem., 91, 6-8 (1987)
- 47. E. S. Smotkin, A. J. Bard, A. Campion, M.A. Fox, T. E. Mallouk, S. E. Webber and J. M. White, "Bipolar TiO2/Pt Semiconductor Photoelectrodes and Multielectrode Arrays for Unassisted Water Splitting". J. Phys. Chem., 90, 4604-4607 (1986)

#### **Book Review**

1. Smotkin, E. S., "Electrochemical Activation of Catalysis: Promotion, Electrochemical Promotion, and Metal Support Interactions" By Costas Vayenas, Symeon Bebelis, Costas Pliangos, Susanne Brosda, and Demetrios Tsiplakides (University of Patras, Patras, Greece). Kluwer Academic/Plenum Publishers: New York. 2001. xxxii + 574 pp. *J. Am. Chem. Soc.*; (Book Review); 2002; 124(51); 15402-15402

#### **Invited Lectures**

- 1. Keynote lecturer: Workshop on Opportunities in Nanocatalysis, Hosted by the Center for Functional Nanomaterials, Brookhaven National Laboratory, Tarrytown House, Tarrytown, New York, October 19-21, 2005
- 2. Dissection of a fuel cell catalyst by XAS, XRD and FTIR, Keynote lecture, Heyrovsky Discussions, Heyrovsky institute, Prague, Czech Republic, June 13, 2005
- 3. Gordon Conference on Fuel Cells, X-ray absorption spectroscopy and FTIR of membrane electrode assemblies in fully operating fuel cells July 25 30, 2004, Bristol, RI
- 4. "The Development of Combinatorial Methods for Discovery of Fuel Cell Electrocatalysts" Olaf A. Hougen Lecturer, University of Wisconsin Hougen Symposium, Department of Chemical Engineering, University of Wisconsin-Madison, September 17 18, 2003
- 5. "Fuel Cells Operating in the "GAP" Temperature Regime", Keynote Lecture: 226th American Chemical Society National Meeting, Fuel Cell Systems and Fuel Processing for Fuel Cell Applications Symposium, New York City, September 11, 2003.
- 6. Correlation of FTIR of CO/(Pt, alloys) with XRD, DFT and XANES Experiments and Simulations, US Army Research Office Sponsored Workshop on Theory and Surface Measurements of Fuel Cell Catalysts, University of Denmark, Lyngby, Denmark, June 17, 2003.
- 7. XRD Analysis of Nanostructured Electrocatalysts: Applications of Vegard's Law, US Army Research Office Sponsored Workshop on Theory and Surface Measurements of Fuel Cell Catalysts, University of Denmark, Lyngby, Denmark, June 16, 2003.
- 8. Correlation of FTIR of CO/(Pt, alloys) with XRD, DFT and XANES Experiments and Simulations, US Army Research Office Sponsored Workshop on Theory and Surface Measurements of Fuel Cell Catalysts, University of Denmark, Lyngby, Denmark, June 17, 2003

- 9. XRD Analysis of Nanostructured Electrocatalysts: Applications of Vegard's Law, US Army Research Office Sponsored Workshop on Theory and Surface Measurements of Fuel Cell Catalysts, University of Denmark, Lyngby, Denmark, June 16, 2003
- 10. High Throughput Screening and Preparation of Fuel Cell System Catalysts, 1st International Conference on Polymer Batteries and Fuel Cells, Jeju Island, Korea, June 2, 2003
- 11. High Throughput Fundamental Studies of Fuel Cell Catalysts, 203rd Meeting Paris, France, Palais des Congres de Paris, May 1, 2003, April 27 May 2, 2003.
- 12. Correlation of FTIR of CO/(Pt Alloys) with DFT and XANES Experiments and Simulations, May 1, 2003, 203rd Meeting Paris, France, Palais des Congres de Paris, April 27 May 2, 2003
- 13. Challenges to DMFC Commercialization, Knowledge Foundation's 5th International Symposium: Small Fuel Cells, New Orleans, LA, May 8, 2003
- 14. Correlation of FTIR of CO/(Pt Alloys) with DFT and XANES Experiments and Simulations, Army Research Office Sponsored Second International Conference on Elementary Processes in Molecule-Metal Surface Interactions, Intercontinental Hotel, San Juan, Puerto Rico, May 7, 2003
- 15. Array Membrane Electrode Assemblies for High throughput Screening of fuel Cell Electrocatalysts, BCC Conference: Fuel Cells 2003, Stamford CT, April 1, 2003
- 16. Combinatorial Discovery of Fuel Cell Electrocatalysts, Department of Energy, Non-Platinum Electrocatalysts Workshop, New Orleans, Louisiana, March 21, 2003
- 17. Laser-Activated Membrane Introduction Mass Spectrometry for High-Throughput Evaluation of Bulk Heterogeneous Catalysts, The Second U.S.-Japan workshop on Combinatorial Materials Science & Technology, Winter Park, CO, December 10, 2002
- 18. Array Membrane Electrode Assemblies for High Throughput Screening of Direct Methanol Fuel Cells, 202nd Meeting of the Electrochemical Society, Salt Lake City, Utah, October 24, 2002
- 19. High Throughput Screening of Fuel Cell System Catalysts, 4th International Symposium on Electrocatalysts: From Theory to Industrial Applications, Villa Olmo, Como, Italy, September 23, 2002
- 20. Deuterium Isotope Analysis of Methanol Oxidation on Mixed Metal Fuel Cell Anode Catalysis, International Catalysis Workshop for Young Scientists (ICWYS-2001) Beijing, China, Sept. 24, 2001
- 21. FTIR, XANES and DFT Calculations On Pt Based Fuel Cell Catalysts, ARO Workshop on Application of First-Principles-Based Computational Methods to the Design of Electrochemical Power Systems, Berkeley, CA August 31, 2001
- 22. Methanol and CO Electrooxidation on Pt, Ru, and Pt based Mixed Metal Catalysts, Chicago National Meeting of the American Chemical Society, August 30, 2001
- 23. Direct Methanol Fuel Cell Catalysis, Knowledge Foundation's Small Fuel Cells and Battery Technologies for Portable Power Applications Renaissance Hotel, Washington, D.C., April 24, 2001
- 24. Combinatorial Discovery of Fuel Cell Catalysts: A Feedback Loop Between Rational Heuristics and High Throughput Screening, The First Japan-US Workshop on Combinatorial Material Science and Technology, Sheraton Maui Hotel Convention Center, Maui, Hawaii, October 2, 2000
- 25. Deuterium Isotope Analysis of Methanol Oxidation Kinetics, The 2000 International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, , Dec 14-19, 2000

- 26. Combinatorial Discovery of New Electrocatalysts for Fuel Cells, Florida Catalysis Conference, University of Florida, April 18, 2000
- 27. Combinatorial Discovery of New Electrocatalysts for Fuel Cells: Optical Screening Methods, Cambridge Healthtech Institute, Engineered Catalysis, New Orleans, Louisiana, December 9 10, 1999
- 28. Combinatorial Discovery of Electrocatalysts for Direct Methanol Fuel Cells, NATO Meeting, Frontiers in Molecular Diversity: From Biology to Material Science" Moscow, Russia, Sept. 19, 1999
- 29. Gordon Conference: Combinatorial Design of Electrocatalysts. New London, NH, June 20-25, 1999
- 30. FTIR and Mass Spectroscopic Analysis of NEMCA Olefin Isomerization Reactions, Electrocatalysis ection at the 12th International Conference on Solid State Ionics. Thessaloniki, Greece, June 8, 1999
- 31. Gordon Conference: Rational and Irrational Routes to Better Electrocatalysts. Ventura, CA, January 1999
- 32. Array Fuel Cells for High Throughput Screening of Electrocatalysts, Department of Chemical Engineering, Notre Dame University, September 30, 2003
- 33. High Throughput Screening and Preparation of Fuel Cell System Catalysts, Kwangju Institute of Science and Technology, Gwangju, Korea, June 5, 2003
- 34. Analytical Methodologies for Combinatorial Discovery of Heterogeneous Catalysts, University of Puerto Rico @ Rio Piedras, July 2001
- 35. Linking Rational Heuristics to Combinatorial Discovery of Electrocatalysts, Bowling Green State University, February 16, 2000
- 36. Polarization Modulated FTIR of CO Adsorbed on Arc-melted Pt, PtRu and PtRuOs Electrode Surfaces, Department of Chemistry, Columbia University, New York, September, 1999
- 37. In-situ FTIR of CO Adsorbed on Arc-melted Pt Alloys, Department of Chemistry, University of Texas at Austin, December, 18, 1998
- 38. High Throughput Screening and Fundamental Studies of Fuel Cell Catalysts, Cabot-Superior MicroPowders, 3740 Hawkins NE, Albuquerque, NM, August 5, 2003

#### **Current and Pending Funding**

- 1. Combinatorial discovery of fuel cell catalysts, Subcontract to NSF-ERC with University of Connecticut, \$350K, 2006-2011, pending
- 2. The Role of Surface and Core Oxide Phases in Electrocatalysis, ARO Grant No. W911NF-05-1-0020, \$497,618, November 2004 2007
- 3. NASA-UPR Center for Nanoscale Materials under NASA grant no. NCC3-1034, Co-PI with Carlos Cabrera, \$350,000 for Smotkin lab, November 2003 November 2008
- 4. DMFC Lifetime Improvement Program (DMFC-LIP), Approved by House of Representatives June 20, 2005, Defense Appropriations Bill (HR 2863) for the Direct Methanol Fuel Cell Lifetime Improvement Program (DMFC-LIP). \$4,000,000 Fiscal year 2006-2007
- 5. Development of XRD Facilities for Combinatorial Discovery of Fuel Cell and Fuel Processor Catalysts at the University of Puerto Rico at Rio Piedras, DURIP Grant, Army Research Office, August, 2003-July 2004, \$83,376 (UPR) Program manager, Richard Paur, ARO 919-549-4208

## **Degrees Granted**

- 1. Ryan Kim, Ph.D. in Chemical Engineering; Laser Activated Membrane Introduction Mass Spectrometry, July, 2005
- 2. Sanghyuk Suh, Ph.D. in Chemical Engineering; Isotopic Studies of Methanol and Formic Acid Oxidation, July 2003
- 3. Viswanathan, Rameshkrishnan, Ph.D. in Chemical Engineering; "In-situ X-Ray absorption and electrochemical study of electrocatalysts for polymer electrolyte membrane (PEM) fuel cells" May 2002
- 4. Gurau, Bogdan, Ph.D. in Chemical Engineering; "Direct methanol fuel cells. Catalysis and engineering aspects" May 2002
- 5. Nayar, Amit, M.S. in Chemical Engineering; "High precision, high throughput evaluation of bulk water-gas-shift catalysts by laser activated membrane introduction mass spectrometry (LAMIMS)" July 2001
- 6. Rao, Upendra, M.S. in Chemical Engineering; "Membrane development for intermediate temperature fuel cell systems" July 2001
- 7. Kernerman, Eugene, M.S. in Chemical Engineering; "The Role of CO<sub>ads</sub> islands in methanol oxidation on Pt anode: Investigation by cyclic voltammetry and deuterium isotope substitution" July 2000
- 8. Salazar, Maria D., Ph.D. in Chemical Engineering; "Cathodic hydrogenation of unsaturated hydrocarbons in a polymer electrolyte fuel cells" July 2000
- 9. Kim, Yongtae, M.S. in Chemical Engineering; "The effect of various plasticizers on the transport and electrochemical properties of high molecular weight PEO-based polymer electrolytes" December 1999
- 10. Liu, Renxuan, Ph.D. in Chemistry; "FTIR surface spectroscopy and electrochemical studies of catalysts for direct methanol fuel cells" May 1998
- 11. Liu, Li, M.S. in Chemistry; "Oxidation of methanol on single phase alloys comprised of Pt, Ru, and Os" July 1998
- 12. Nie, Weiguo, M.S. in Chemistry; "Methanol electro-oxidation and methanol crossover in direct methanol fuel cells" May 1996